

Electrochemistry

Topic 09: Redox



Adapted from Scheffler
Lincoln HS, Portland OR

Electrochemistry

Electrochemistry is the study of chemical reactions that generate electrical effects and of the chemical reactions that are caused by the action of an electrical current or applied potential



Oxidation and Reduction

- ◆ Oxidation = loss of electrons.
- ◆ Reduction = gain of electrons.
- ◆ Oxidizing agent = substance that causes oxidation to occur. The oxidizing agent is reduced.
- ◆ Reducing agent = substance that causes reduction to occur. The reducing agent is oxidized.



Electrical Terminology

- ◆ Electrical current may be either **direct (DC)**. or **alternating (AC)**.
- ◆ In **direct current** the electrons flow in a single direction from negative to positive.
- ◆ In an **alternating current** the direction of current flow changes periodically. In the USA there are 60 cycles per second. European electricity is at 50 cycles.
- ◆ A location that has an **excess of electrons** has a **negative charge**. A location that has a **deficiency of electrons** has a positive charge.
- ◆ The rate of **current flow** is measured in **amperes**.
- ◆ The difference in **electrical potential** is measured in **volts**.
- ◆ The **resistance** to current flow is measured in **ohms**.

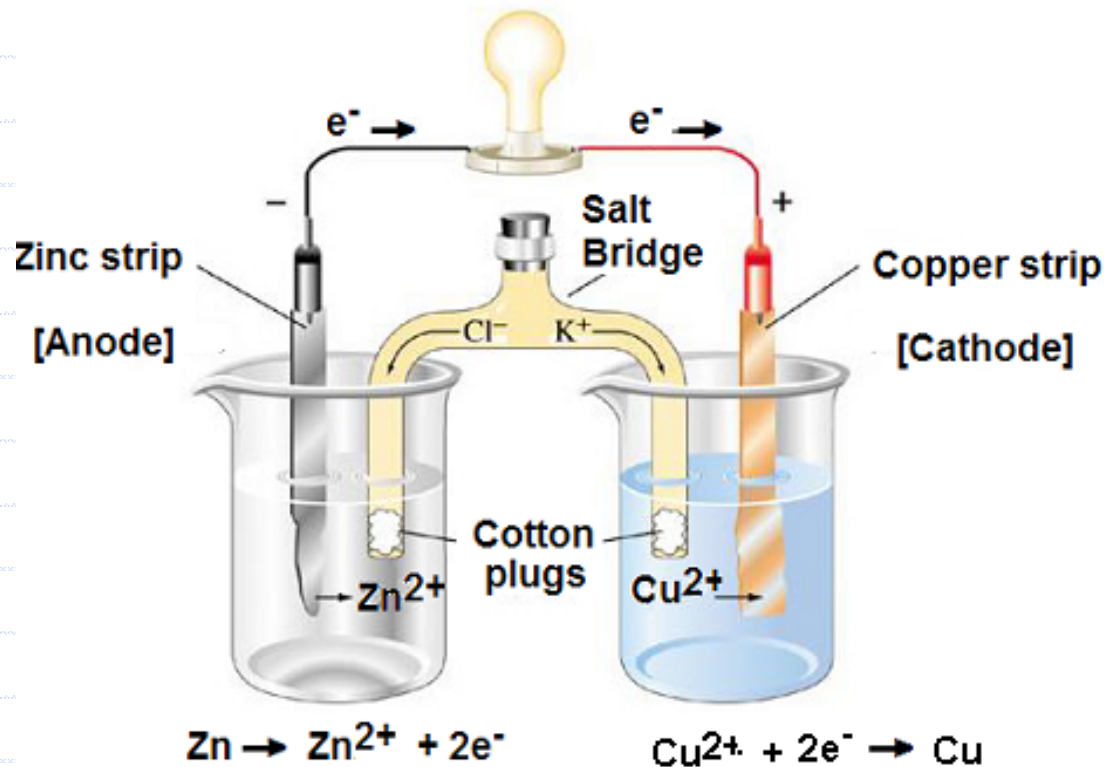


Electrochemical Cells

- ◆ An **electrical current** can be produced from a harnessed chemical reaction.
- ◆ This system is known as an electrochemical cell
- ◆ Voltaic cells are also known as **galvanic cells** or simply as **voltaic cells**.



Example 1: The Daniel Cell



The copper electrode is placed in a solution of Cu^{2+} such as copper (II) sulfate or copper (II) nitrate.

The zinc electrode is placed into a solution of Zn^{2+} ion such as zinc sulfate or zinc nitrate.

The two sides are connected with a U tube containing an electrolyte such as KCl or KNO_3 . This structure is called a **salt bridge**.

Daniel Cell

Cells and Cell Reactions in a Daniel Cell

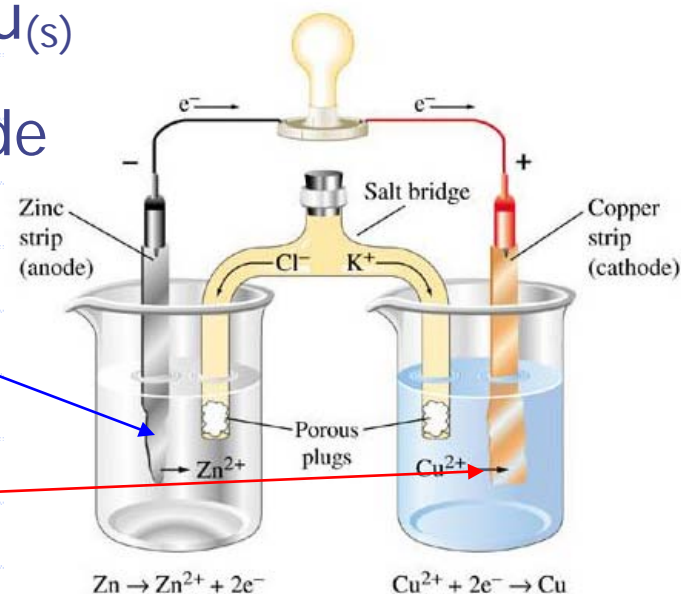
◆ Overall reaction



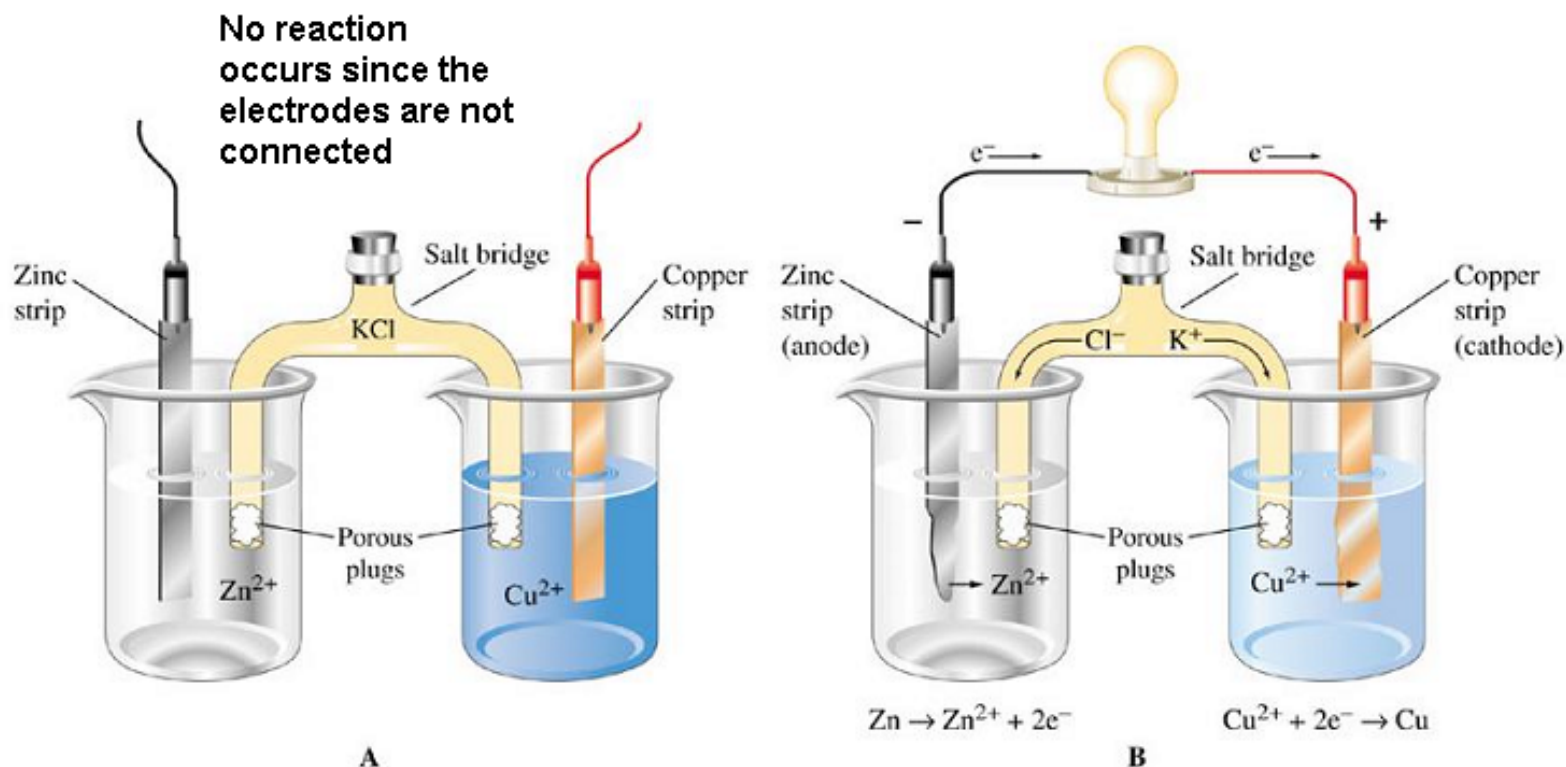
◆ Oxidation half reaction at the anode



◆ Reduction half reaction at the cathode



Electrochemical Cells



The voltaic cell on the left has a Potential difference of about 1.1 volts

The addition of the external circuit containing the light bulb results in a current flow through the circuit. Oxidation and reduction now occur



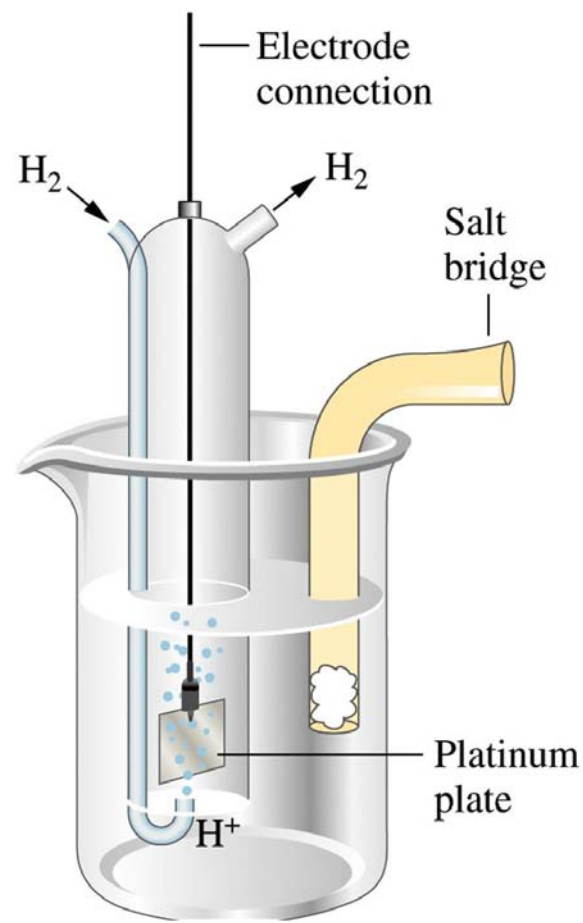
A Standard Hydrogen Electrode

- ◆ A **hydrogen electrode** consists of a platinum electrode covered with a fine powder of platinum around which $\text{H}_2(\text{g})$ is bubbled.
- ◆ Its potential is defined as zero volts.
- ◆ It is the reference point for potential measurements

Hydrogen Half-Cell



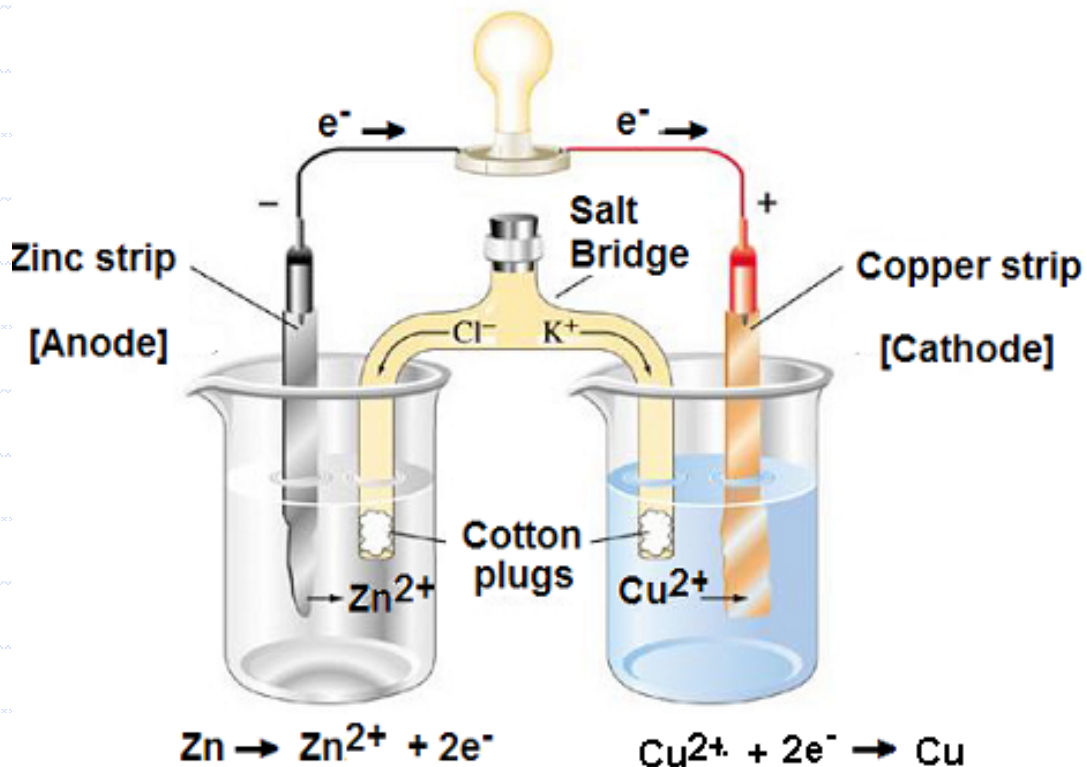
A reversible reaction



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Distinguishing the Anode and Cathode



◆ Oxidation occurs at the anode

◆ Reduction occurs at the cathode

Oxidation (loss of e^-)

Reduction (gain of e^-)

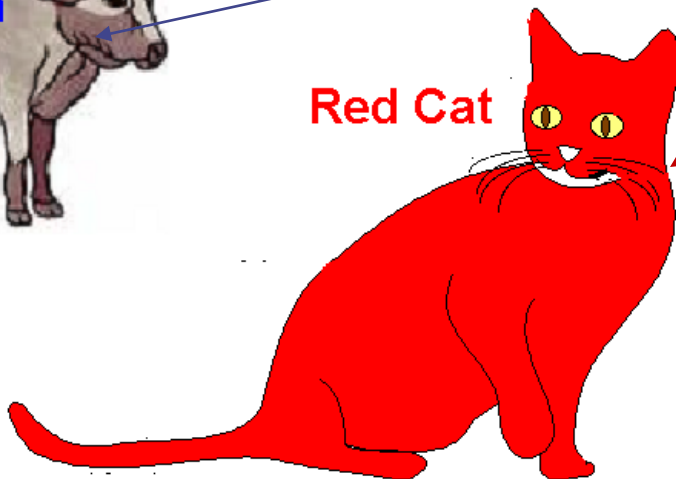


Distinguishing the Anode and Cathode



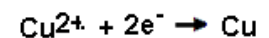
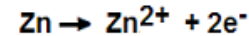
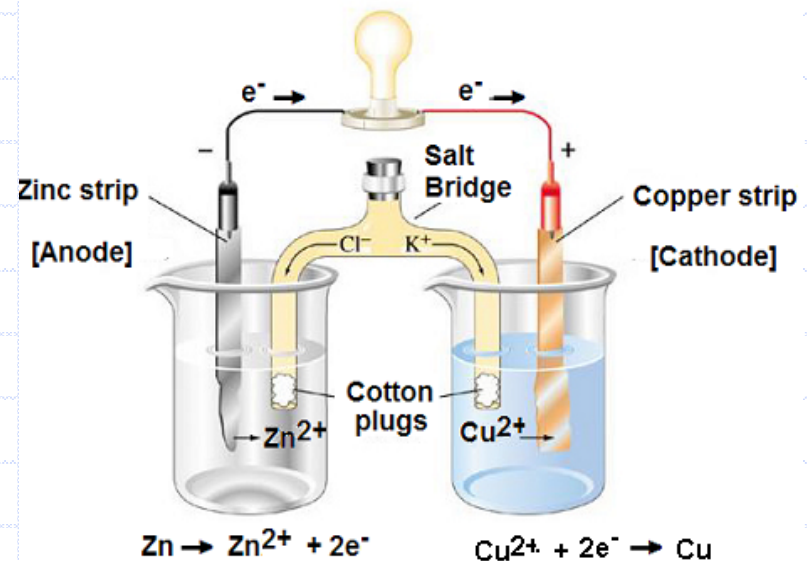
An Ox

Red Cat



◆ Oxidation occurs at the anode

◆ Reduction occurs at the cathode

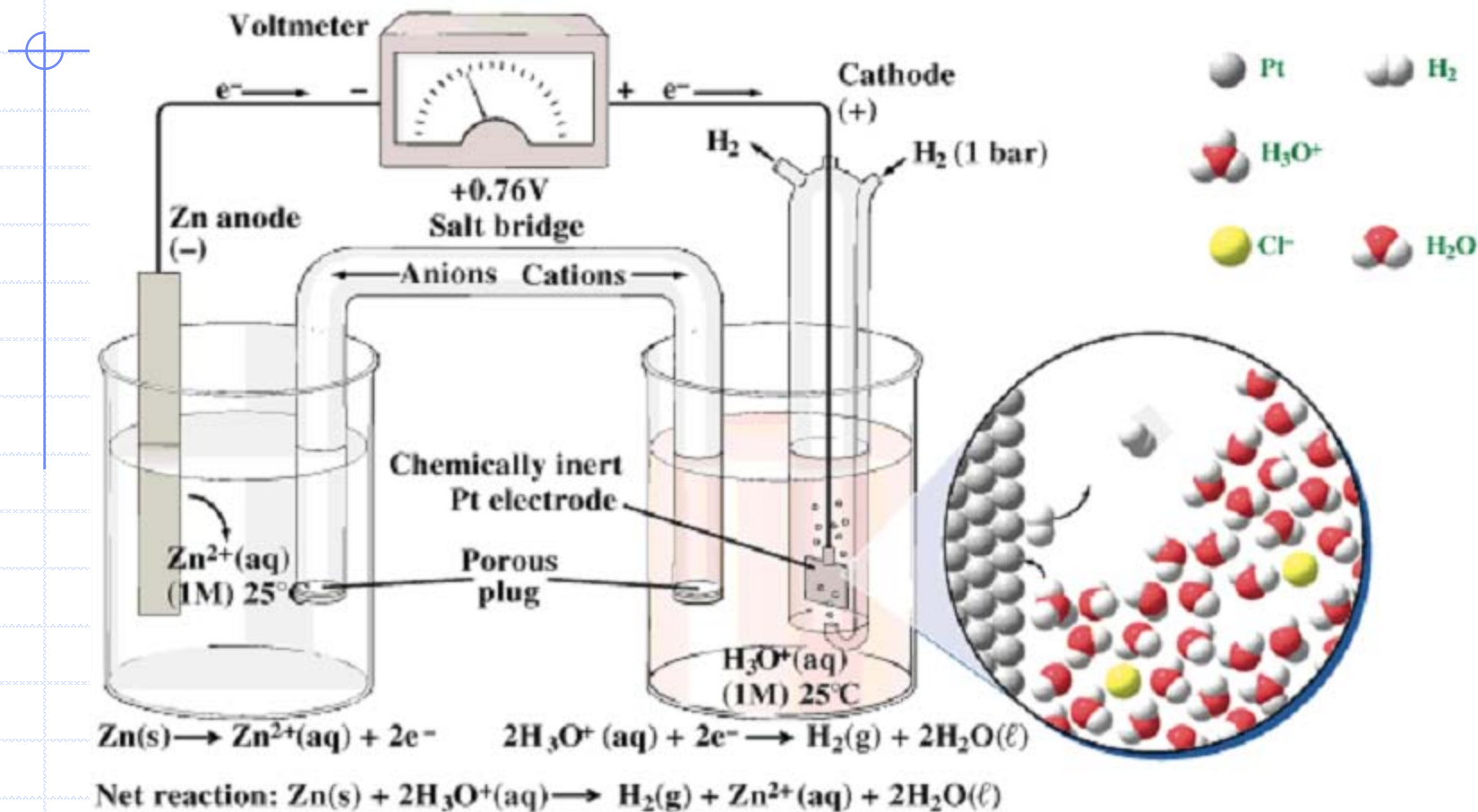


Oxidation (loss of e^{-})

Reduction (gain of e^{-})



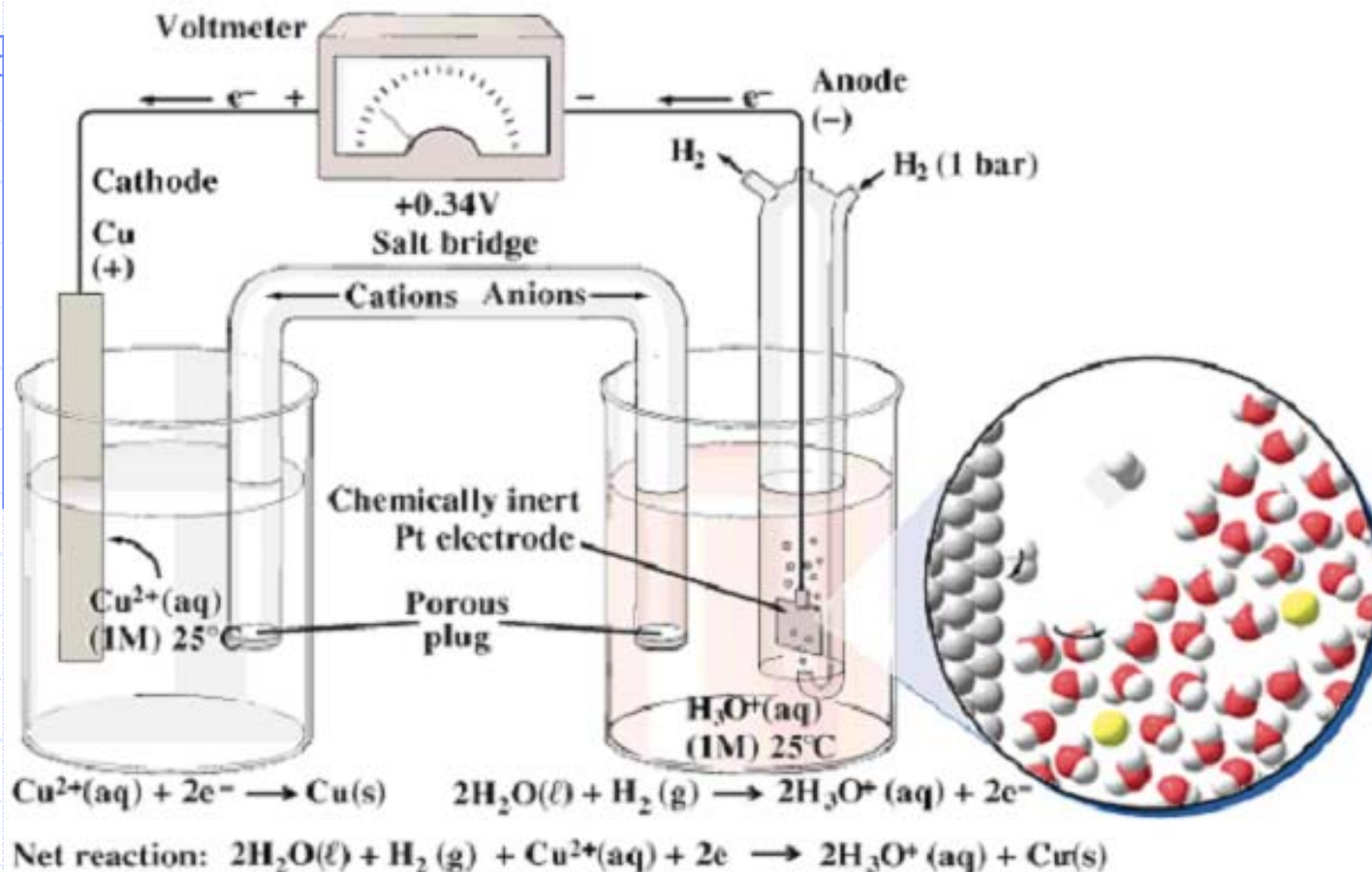
Standard Reduction Potentials



Zinc when paired with a standard hydrogen electrode as the **cathode** produces an electrode potential of 0.76 volts.



Standard Reduction Potentials



Copper when paired with a standard hydrogen electrode as the anode produces an electrode potential of 0.76 volts.



Standard Reduction Potentials

- ◆ The standard conditions for electrochemical cell reactions are
 - 25°C
 - 1M concentrations for all ions
 - 1 atmosphere pressure for all gases
- ◆ The standard reduction potential table shows the reduction potentials at these conditions relative to hydrogen for various reduction of a half-reactions



Standard Reduction Potentials

(See Table 14, page 12 in your Chemistry Data Booklet)

$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	- 3.05 v
$\text{Mg}^{+2} + 2 \text{e}^- \rightarrow \text{Mg}$	- 2.37 v
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66 v
$\text{Zn}^{+2} + 2 \text{e}^- \rightarrow \text{Zn}$	- 0.763 v
$\text{Fe}^{+2} + 2 \text{e}^- \rightarrow \text{Fe}$	- 0.440v
$2 \text{H}^+_{(\text{aq})} + 2 \text{e}^- \rightarrow \text{H}_{2(\text{g})}$	0.00v
$\text{Cu}^{+2} + 2 \text{e}^- \rightarrow \text{Cu}$	+0.337v
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.799v
$\text{O}_{2(\text{g})} + 4 \text{H}^+_{(\text{aq})} + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}_{(\text{l})}$	+1.229v
$\text{F}_2 + 2\text{e}^- \rightarrow 2 \text{F}^-$	+ 2.87v



Application Question 1:

If the reduction of mercury (I) in a voltaic cell is desired, the half reaction is:



Which of the following reactions could be used as the anode (oxidation)?



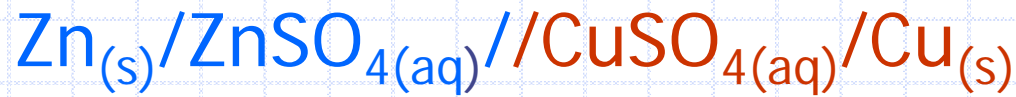
Using Cell Potentials

- ◆ They show the potential difference, in volts, between the electrodes of an electrochemical cell.
- ◆ They indicate the direction of Oxidation-Reduction reactions.
- ◆ A positive value indicates a spontaneous reaction indicates that the direction is positive.



Shorthand Notation for Electrochemical cells

◆ The shorthand representation of an electrochemical cell showing the two half-cells connected by a salt bridge or porous barrier, such as:



anode

cathode

The electrodes are shown on the ends and the electrolytes for each side are shown in the middle.



Calculating Cell Potentials From Standard Reduction Potentials

◆ Calculate the cell potential for a cell made from silver and zinc electrodes.

From the standard reduction table



Since there must be one oxidation and one reduction, the direction of one of two half reactions above must be reversed.

Reversing the zinc half reaction making it the oxidation would yield a positive cell potential



Cell potential = 1.562 volts



Application Question 2



◆ Does Zn react with Mg^{2+} ?

◆ Does Mg react with Zn^{2+} ?

If Mg is oxidized $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^{-} \quad E^{\circ} = +2.37 \text{ v}$

Combining this with the reduction of $\text{Zn}^{2+} \quad E^{\circ} = -0.76 \text{ v}$

Leaves an overall positive cell potential $+1.66 \text{ v}$

Therefore Mg reacts with Zn^{2+} .

Zn does not react with Mg^{2+}



Metal Displacement Reactions

- ◆ The electrochemical cell potentials form the basis for predicting which metals will react with salt solution of other metals
- ◆ This order of reactivity of metals in single replacement reactions is called the activity series
- ◆ The solid of more reactive metals will displace ions of a less reactive metal from solution.
- ◆ The relative reactivity of metals is based on potentials of half reactions.
- ◆ Elements with very different potentials react most vigorously.



The Activity Series

K	$K^+ + e^- \rightarrow K$	-2.93
Ca	$Ca^{2+} + 2 e^- \rightarrow Ca$	-2.87
Na	$Na^+ + e^- \rightarrow Na$	-2.71
Mg	$Mg^{2+} + 2 e^- \rightarrow Mg$	-2.37
Al	$Al^{3+} + 3 e^- \rightarrow Al$	-1.66
Zn	$Zn^{2+} + 2 e^- \rightarrow Zn$	-0.763
Fe	$Fe^{2+} + 2 e^- \rightarrow Fe$	-0.440
Sn	$Sn^{2+} + 2 e^- \rightarrow Sn$	-0.136
Pb	$Pb^{2+} + 2 e^- \rightarrow Pb$	-0.126
H	$2 H^+ + 2 e^- \rightarrow H_2$	0.000
Cu	$Cu^{2+} + 2 e^- \rightarrow Cu$	+0.337
Ag	$Ag^+ + e^- \rightarrow Ag$	+ 0.799

- Elements with highly negative reduction potentials are not easily reduced but they are easily oxidized.
- Since metals react by being oxidized the more negative the reduction potential the more reactive the element.
- Elements higher in the table (*more negative potential*) can displace any element lower (*more positive potential*).
- So $Zn + CuCl_2 \rightarrow ZnCl_2 + Cu$
 $Cu + ZnCl_2 \rightarrow$ No Reaction



The activity Series is really a reduction potential table arranged from negative to positive

Gibbs Free Energy and Cell Potential

$$\Delta G = -nFE = RT \ln Q$$

where n = number of electrons changed

F = Faraday's constant

E = cell potential



The Nernst Equation -- Effect of Concentration on Cell Voltage:

Takes into account corrections for systems that are not operating at standard conditions

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (RT/nF) \ln Q$$

Where: $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

T = Kelvin temperature

n = moles of electrons transferred

F = Faraday's constant = $96,500 \text{ C mol}^{-1}$

Q = reaction quotient
= $[\text{products}]/[\text{reactants}]$

and $1 \text{ J C}^{-1} = 1 \text{ volt}$



The Nernst Equation – An Alternate Form

If the temperature is fixed at 298 K and the natural log is replaced with a common log an alternate form for the Nernst equation can be written as follows:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0591/n)\log Q$$

Where: n = moles of electrons transferred

Q = reaction quotient

= [products]/[reactants]

The alternate form of the Nernst equation may be a little easier to use, but it is less versatile since the temperature must be fixed at standard thermodynamic temperature



The Nernst Equation – Sample Problem 1

What is the cell potential for the Daniel's cell when the $[Zn^{+2}] = 10 [Cu^{+2}]$? Assume the temperature is $25^{\circ}C$.

$$Q = ([Zn^{+2}]/[Cu^{+2}]) = (10 [Cu^{+2}])/[Cu^{+2}] = 10$$

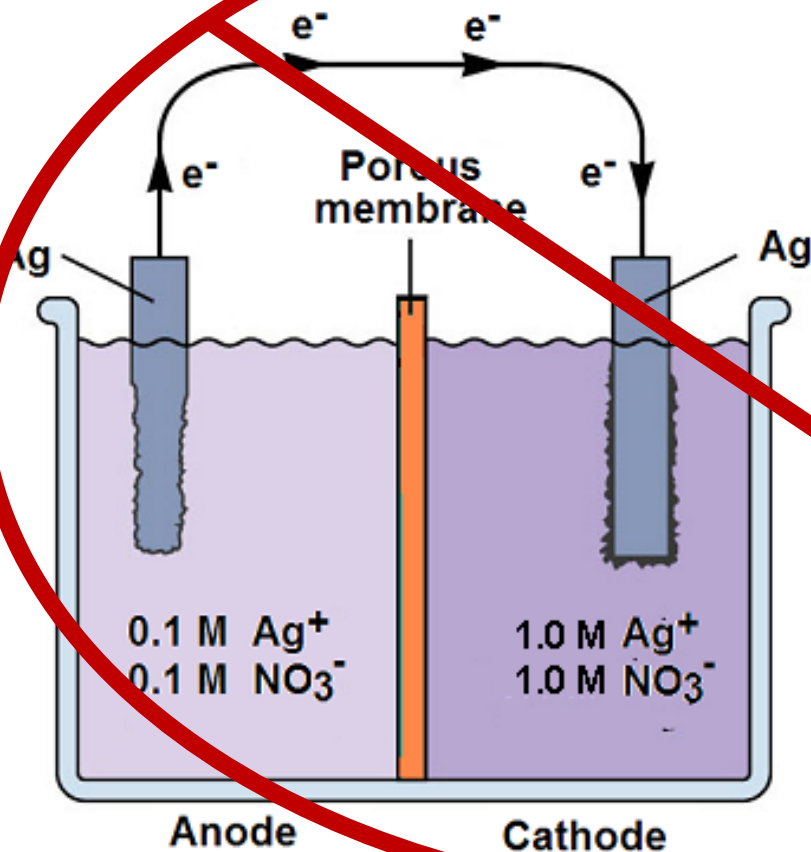
$E^{\circ} = (0.34 \text{ V})_{Cu \text{ couple}} + (-(-0.76 \text{ V})_{Zn \text{ couple}}) = 1.10 \text{ Volts}$
and $n = 2$ since 2 electrons are transferred between Zinc and copper

thus
$$E_{cell} = 1.10 \text{ V} - \frac{(8.314 \text{ J mol}^{-1}\text{K}^{-1})(298\text{K}) (\ln 10) \text{ V}}{(96,500 \text{ C mol}^{-1})(2)}$$

$$E_{cell} = 1.100\text{V} - 0.0296\text{V} = 1.074 \text{ V}$$



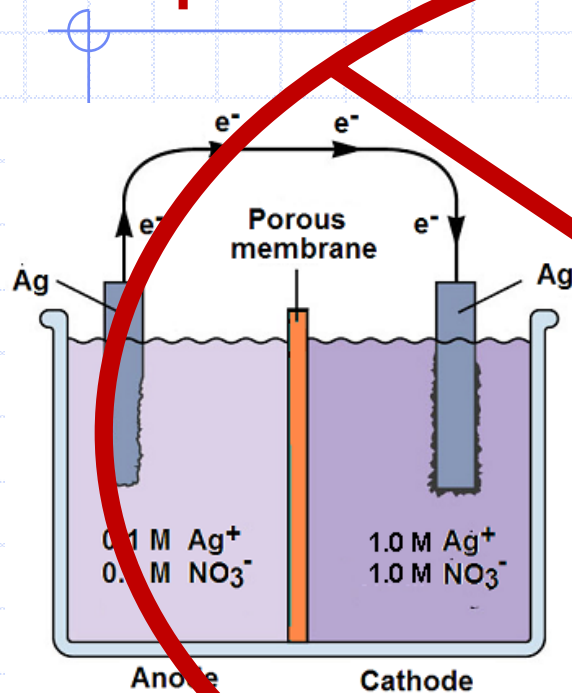
Concentration and the Nernst Equation



◆ In the diagram at the left the half cell reactions are the same but the concentrations are different

◆ Will there be electron flow?

Concentration and the Nernst Equation



$$Q = \frac{[\text{Ag}^+]_{\text{anode}}}{[\text{Ag}^+]_{\text{cathode}}} = \frac{0.1}{1} = 0.1$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{(0.0591/n) \log(Q)}{1}$$

0 V 1

$$E_{\text{cell}} = - (0.0591) \log(0.1) = 0.0591 \text{ V}$$



Batteries Are Applications of Electrochemical Cells

Batteries

- device that converts chemical energy into electricity

Primary Cells

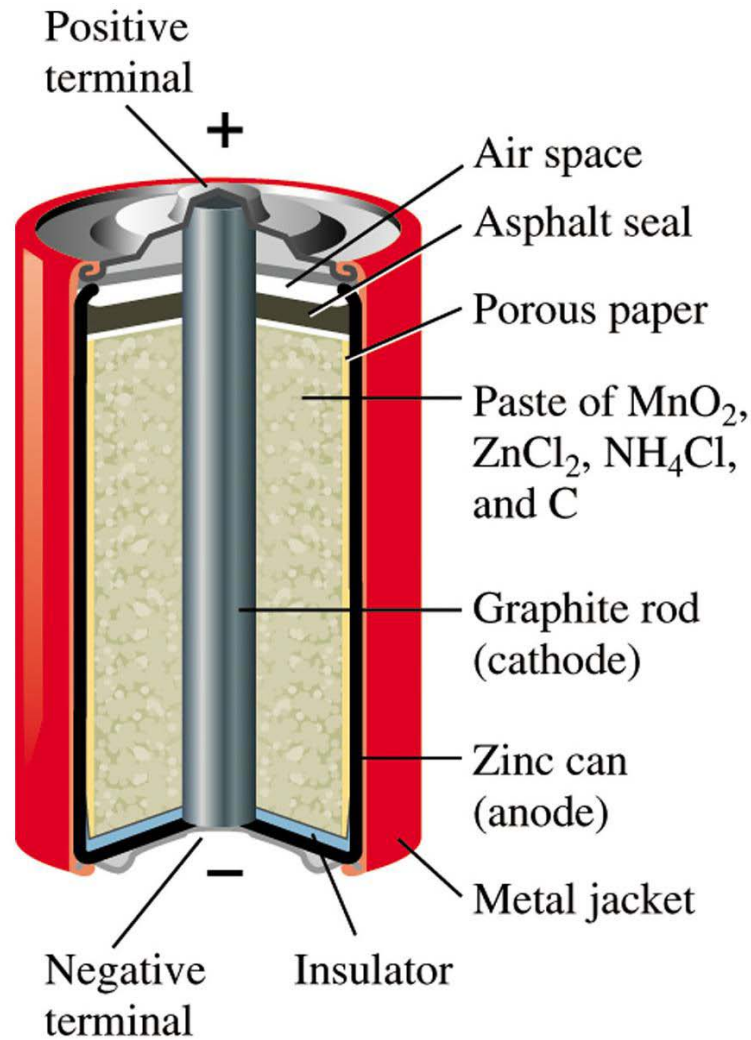
- non-reversible electrochemical cell
- non-rechargeable cell

Secondary Cells

- reversible electrochemical cell
- rechargeable cell



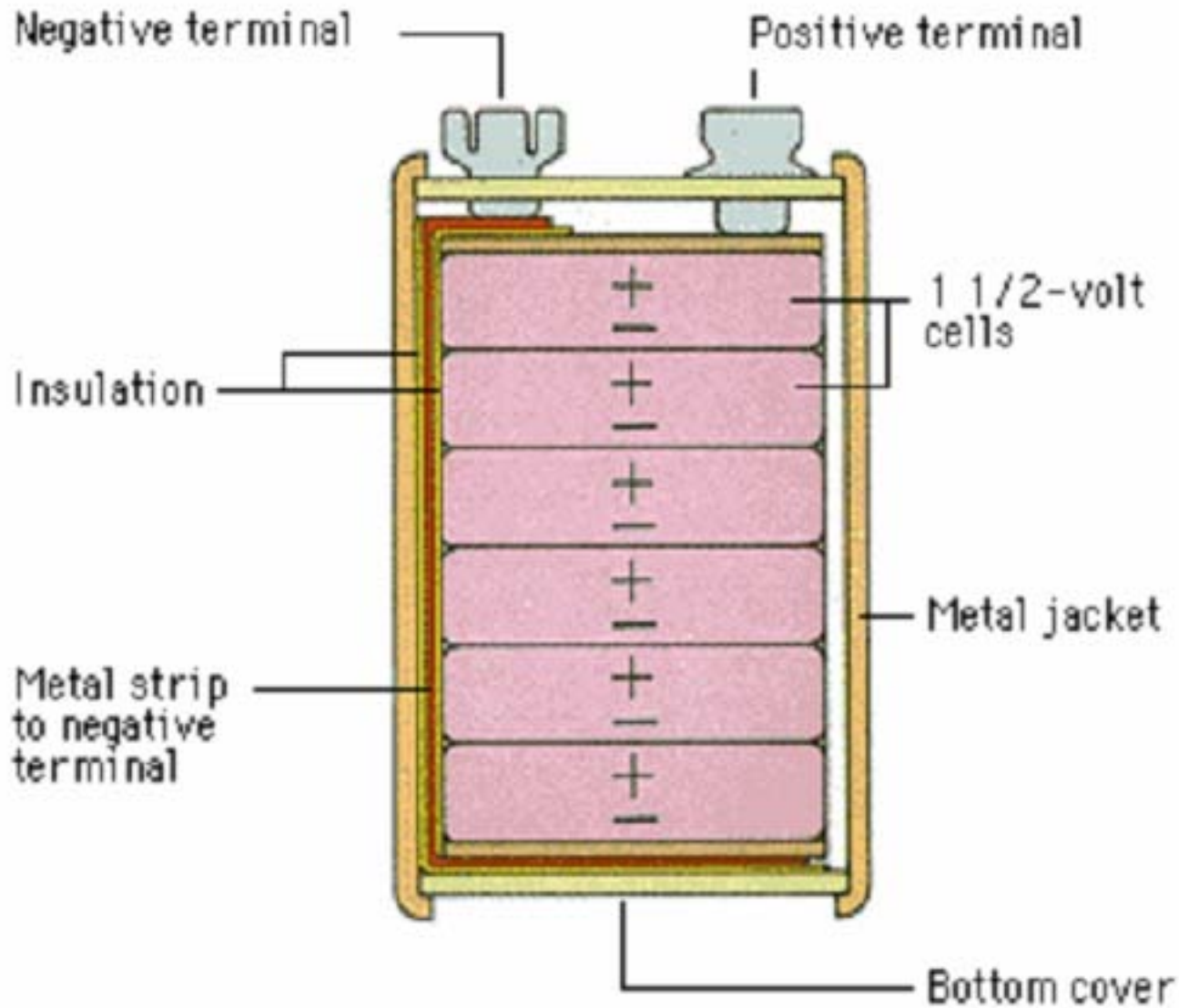
A Common Dry Cell



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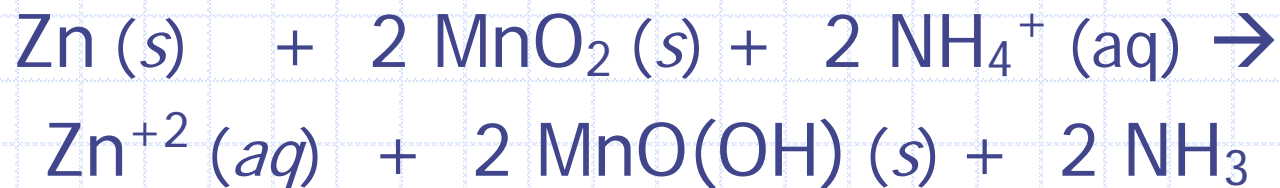


A 9 Volt Dry Cell

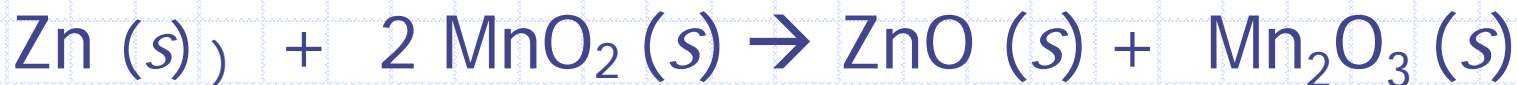


"Flash Light" Batteries

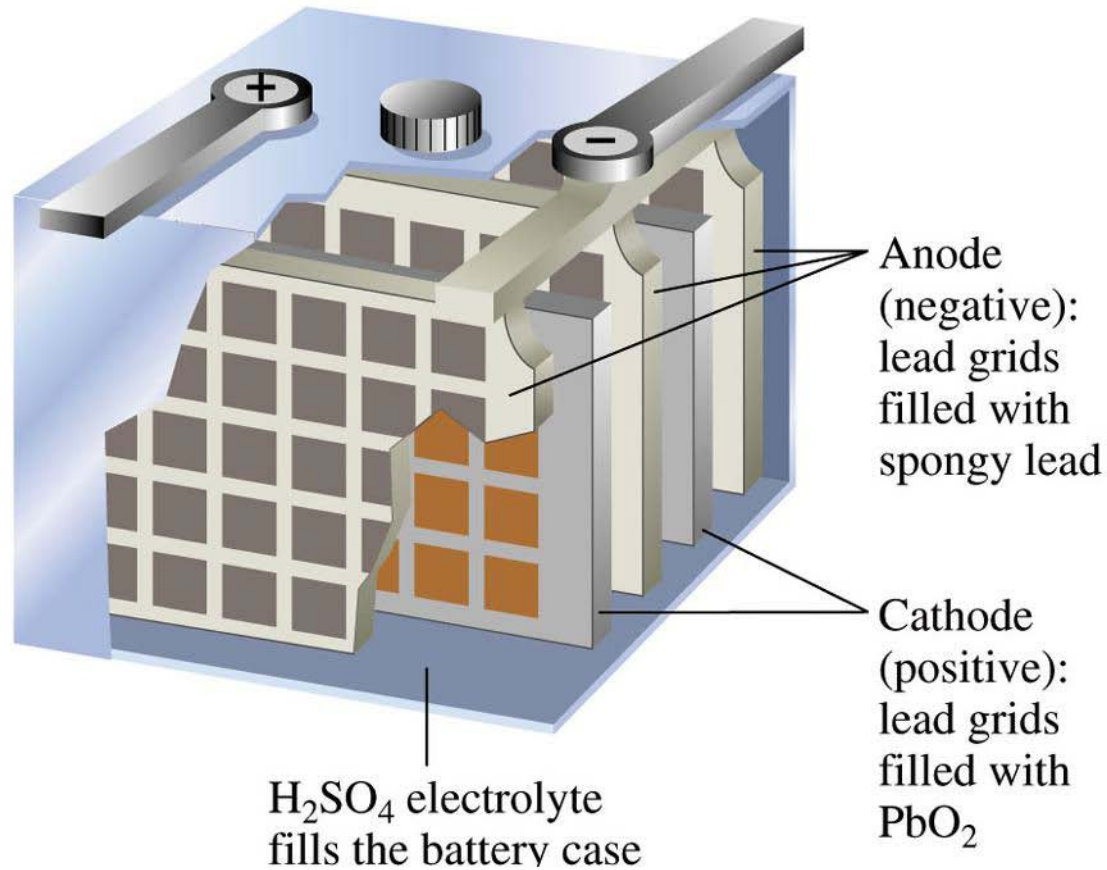
Dry Cell



Alkaline Cell



Lead-Acid (Car Battery)



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Lead-Acid (Car Battery)

Overall reaction

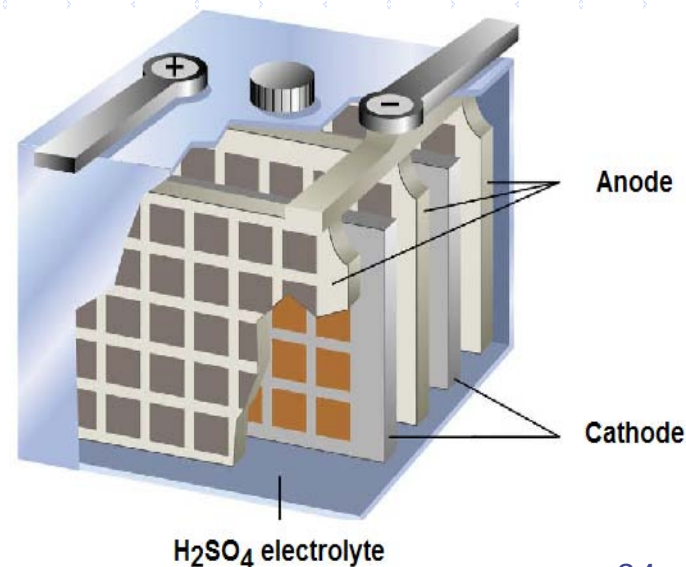


$E = 2.0$ - volts per cell

Cathode



Anode



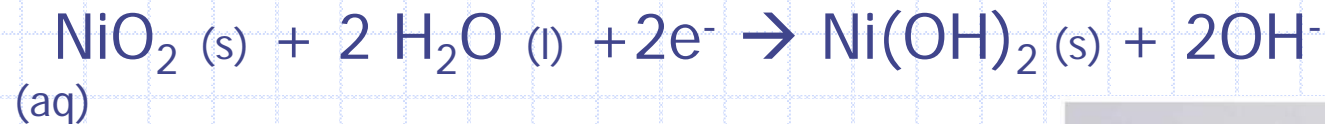
Nickel-Cadmium (Ni-Cad)

Overall reaction



$$E_{\text{NiCad}} = 1.25 \text{ v/cell}$$

Cathode



Anode



Electrolysis



Electrolysis

- ◆ An electrolysis is the inverse of an electrochemical cell.
- ◆ A non-spontaneous reaction is caused by the passage of an electric current through a solution.
- ◆ By passing a DC current through an electrolyte, the reaction can be made to proceed in the reverse or non-spontaneous direction.

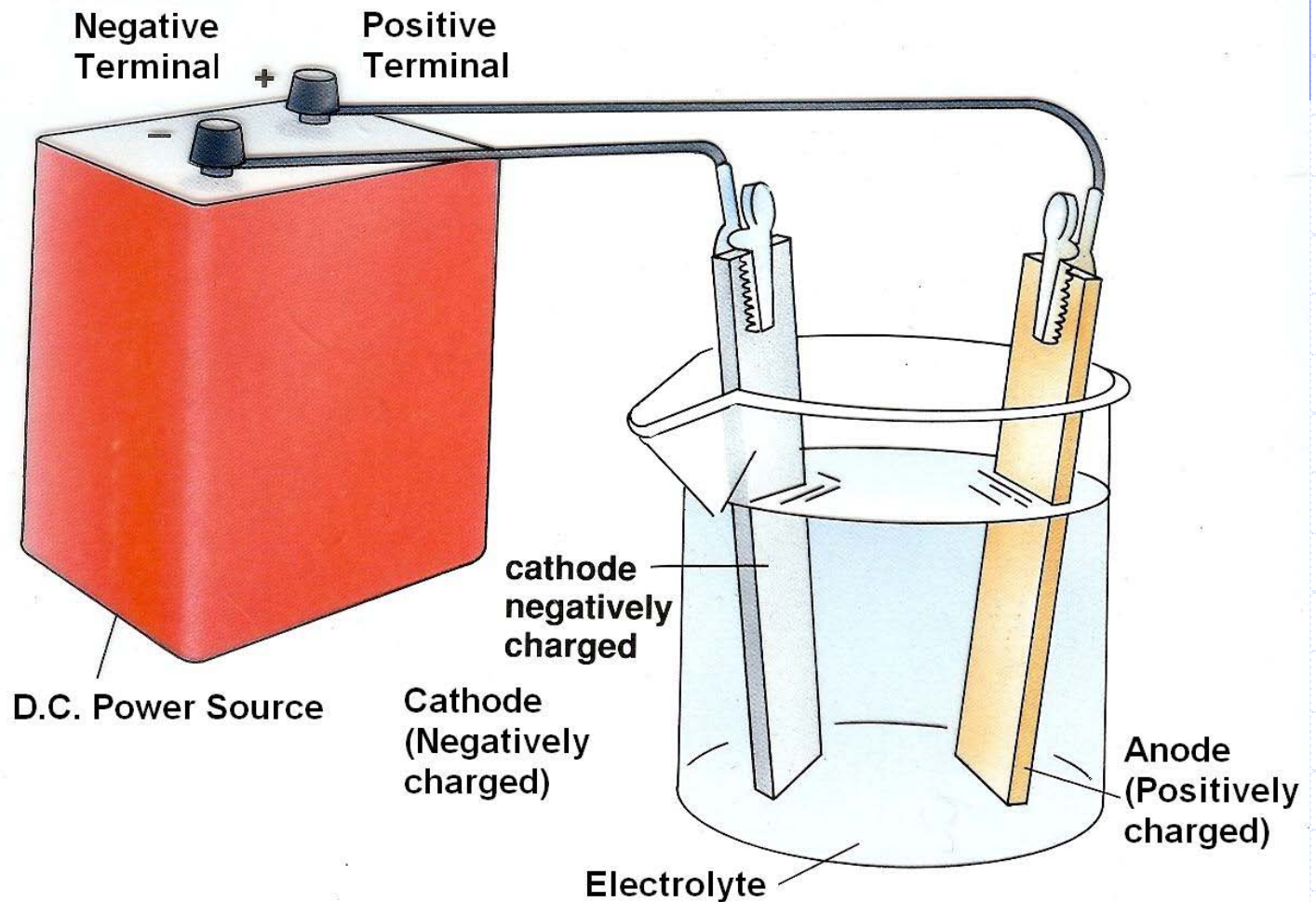


Electrolysis

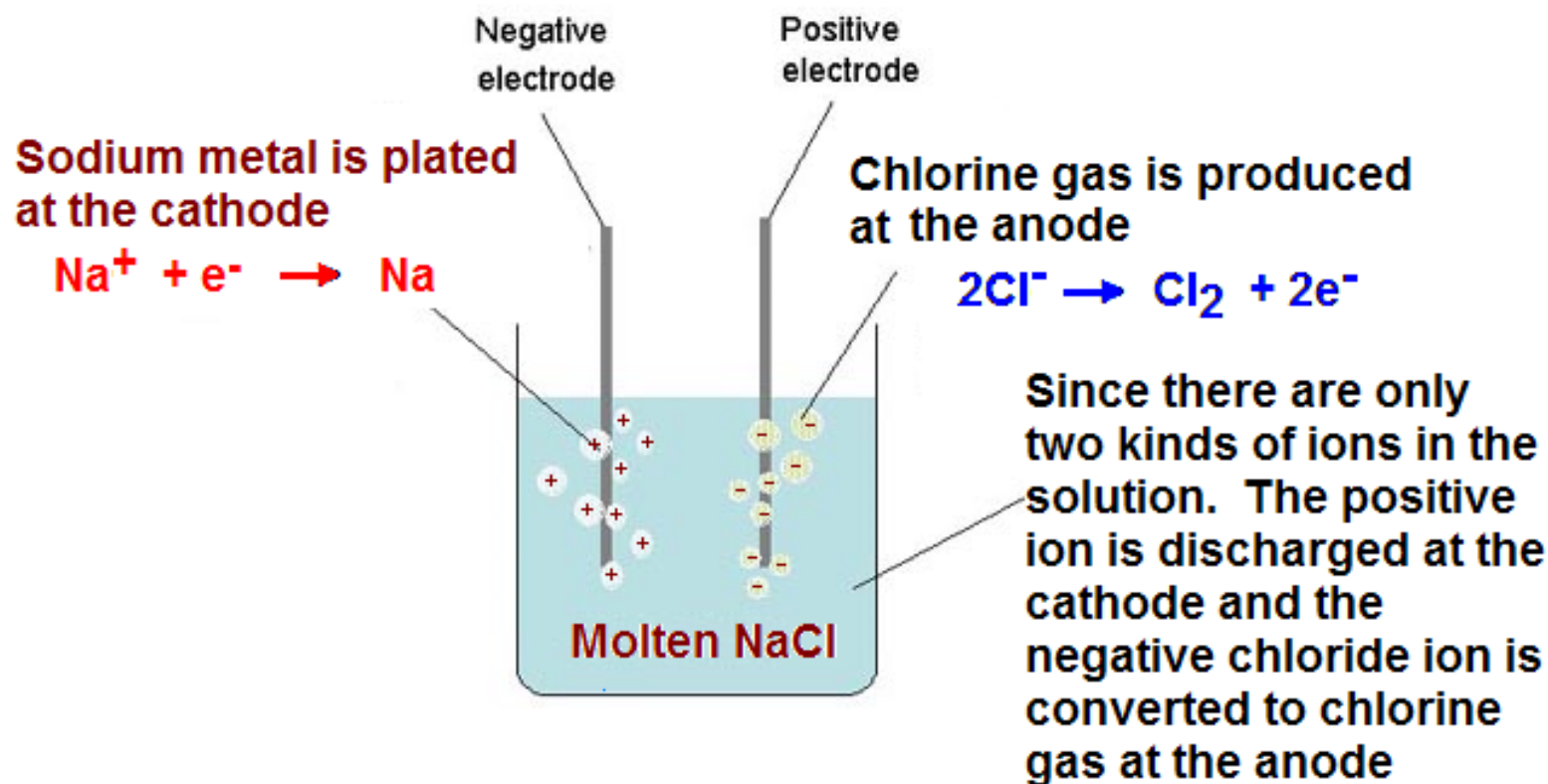
- ◆ The reactions at the anode and cathode depend on the relative reduction potentials of the solute and the solvent.
- ◆ The substance produced at the cathode depends on the cation that has the higher (more positive) reduction potential.
- ◆ The substance produced at the anode depends on the cation that has the lower (more negative) reduction potential.



Diagram of a Simple Electrolysis



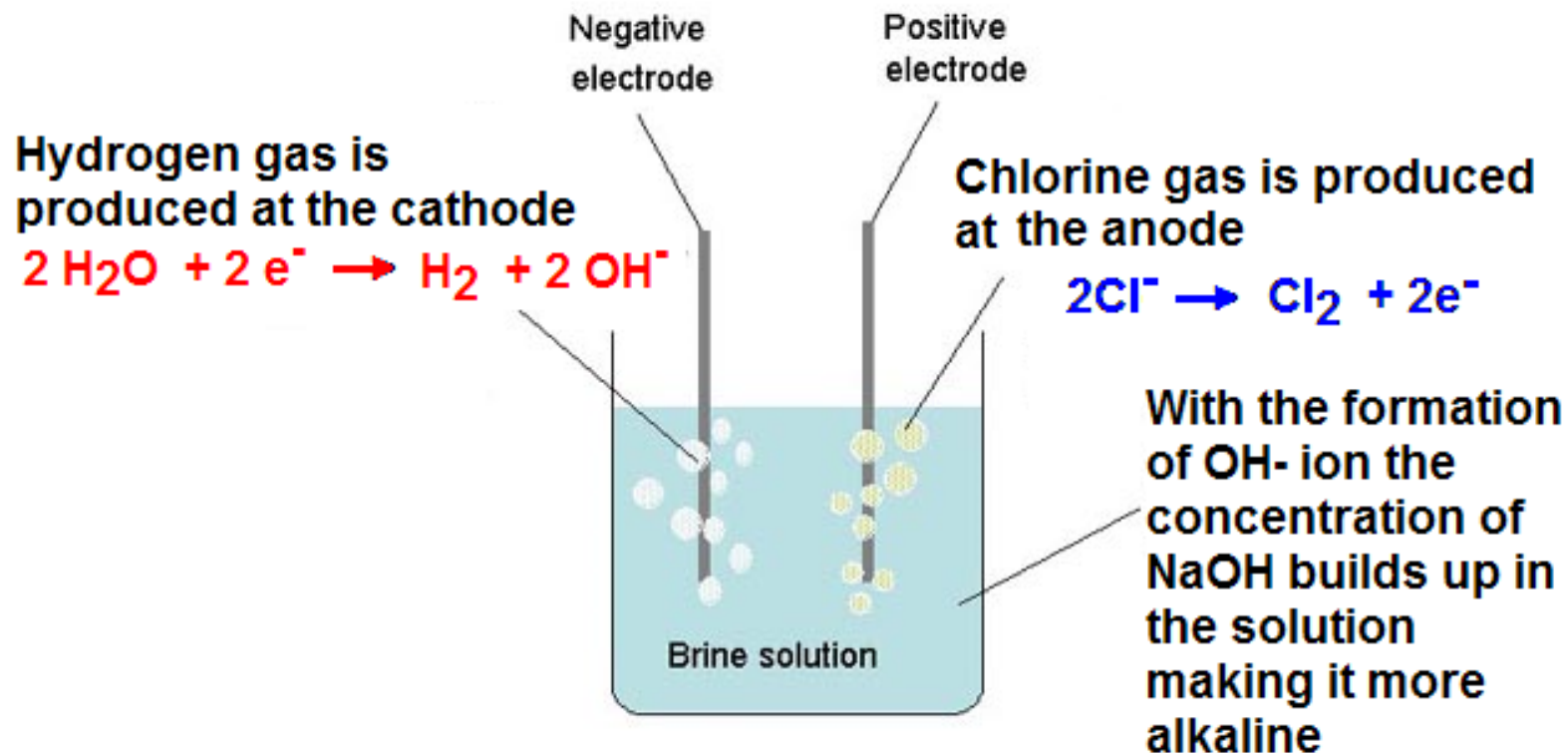
Electrolysis of Molten NaCl



If sodium chloride is heated to its melting point, then the resulting liquid contains mobile ions. This is a way of producing sodium metal.



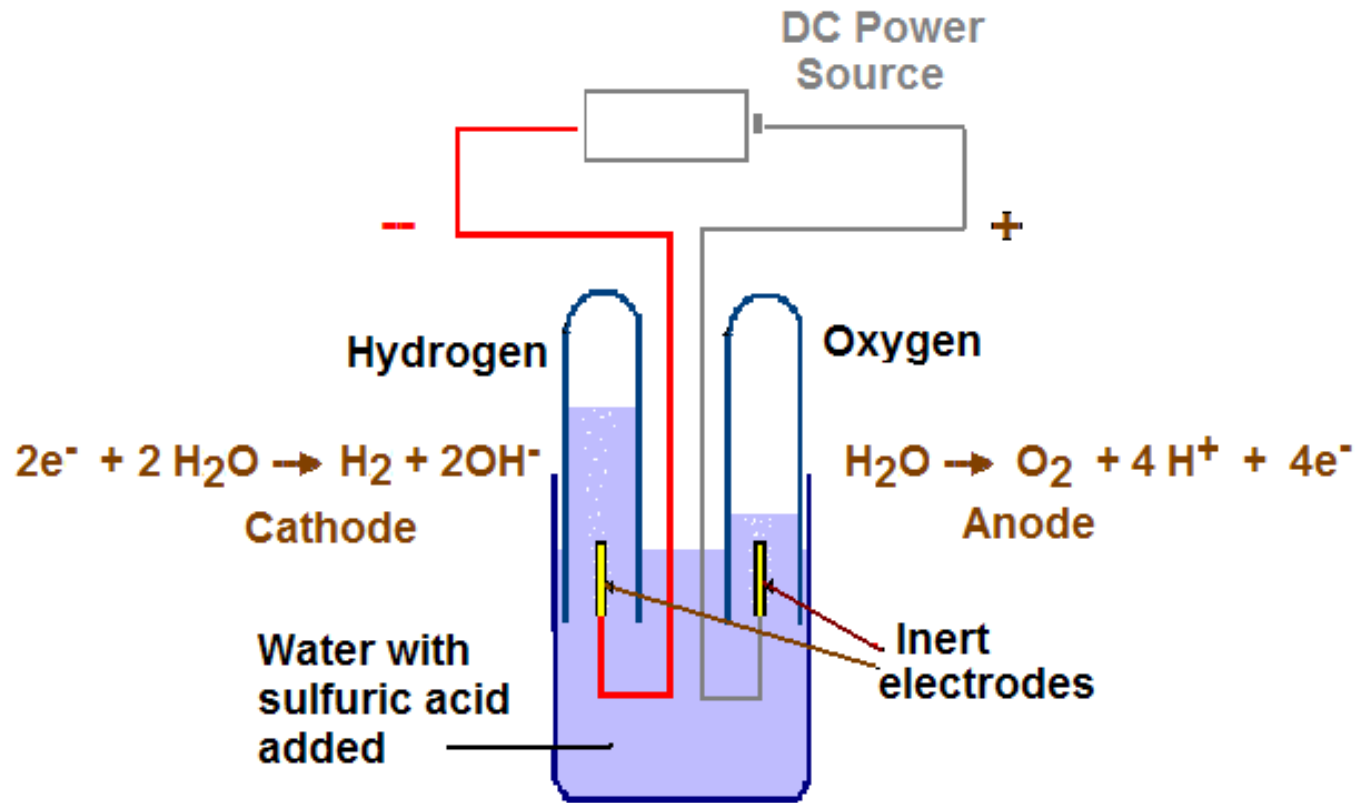
Electrolysis of Brine



The electrolysis of brine solution results in the reduction of water to hydrogen gas rather than sodium ion to sodium metal



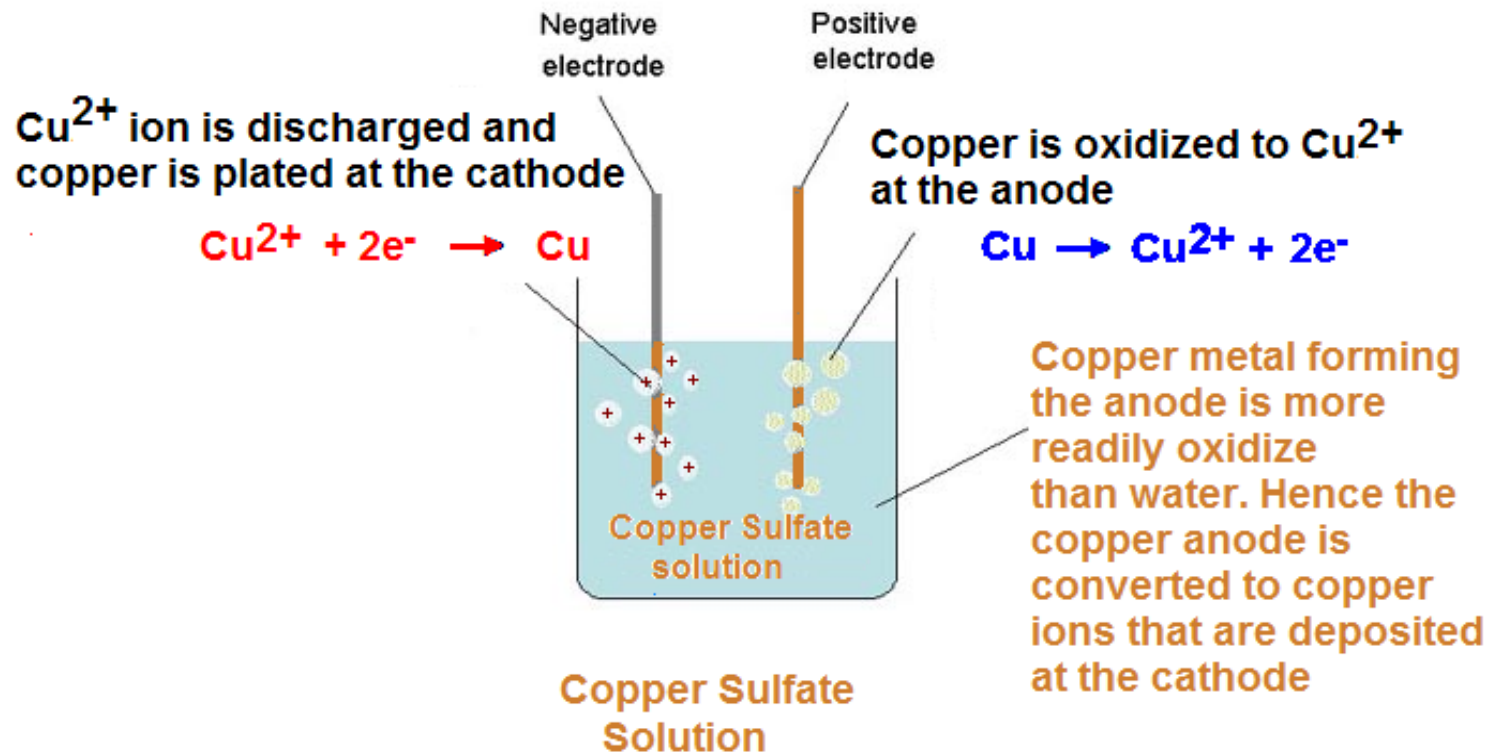
Electrolysis of Water



The electrolysis of water requires a small amount of sulfuric acid to be added. Hydrogen and oxygen are produced in a 2 to 1 ratio.



Electrolysis of copper sulfate with a copper electrodes



To electroplate a metal, the object to be plated is made the cathode and the metal to be plated is the anode. The electrolyte is a solution containing the cation to be plated.



Electrolysis Calculations

The amount of a substance produced during the electrolysis reaction depends on the current applied and the time the reaction is allowed to run

- ◆ 1 coulomb = 1 ampere second
- ◆ 1 mole e^- = 96,500 coulombs = 1 Faraday

Any combination of current and time that will result in 1 Faraday of charge will produce 1 mole of electrons.



Sample Problem 1

Example 1: How many grams of chromium can be plated from a Cr^{+6} solution in 45 minutes at a 25 amp current?

$$= \frac{(45 \text{ min}) (60 \text{ s min}^{-1}) (25 \text{ amp}) (1 \text{ mol e}^{-}) (52 \text{ g mol}^{-1} \text{Cr})}{(96,500 \text{ amp s}) (6 \text{ mol e}^{-} \text{ mol}^{-1} \text{Cr})}$$



Sample Problem 1

Example 1: How many grams of chromium can be plated from a Cr^{+6} solution in 45 minutes at a 25 amp current?

$$\begin{aligned} &= \frac{(45 \text{ min}) (60 \text{ s min}^{-1}) (25 \text{ amp}) (1 \text{ mol e}^-)(52 \text{ g mol}^{-1} \text{ Cr})}{(96,500 \text{ amp s}) (6 \text{ mol e}^- \text{ mol}^{-1} \text{ Cr})} \\ &= 58 \text{ g Cr} \end{aligned}$$



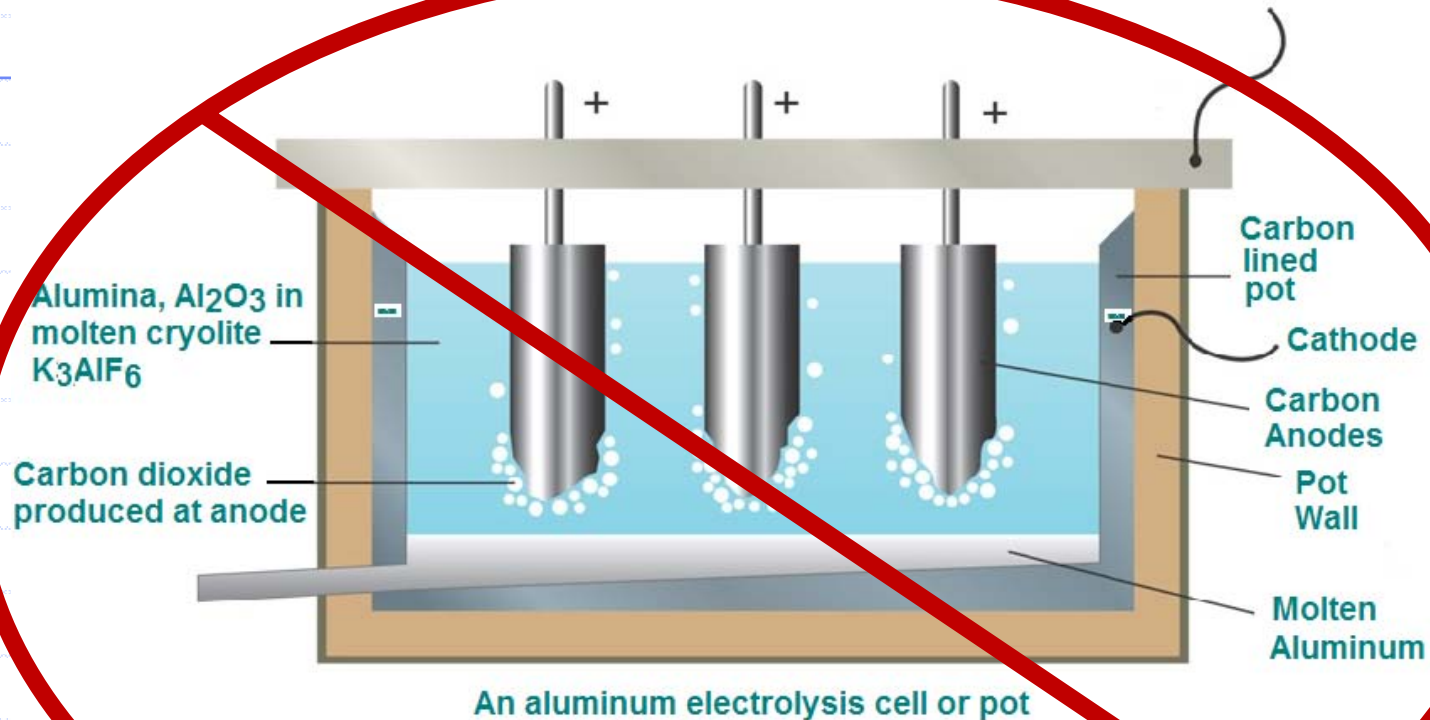
Electrolysis Applications

Preparation of Aluminum (Hall-Heroult process)

- The industrial production of aluminum is accomplished by the electrolysis of relatively pure alumina
- This process was first invented in France in 1886 by Paul Heroult and at almost the same time in the United States by Charles Hall.
- Adding cryolite, Na_3AlF_6 , to alumina results the mixture can be made to melt at 980°C . rather than the more than 2000°C of alumina alone.
- It is then electrolyzed using graphite electrodes.

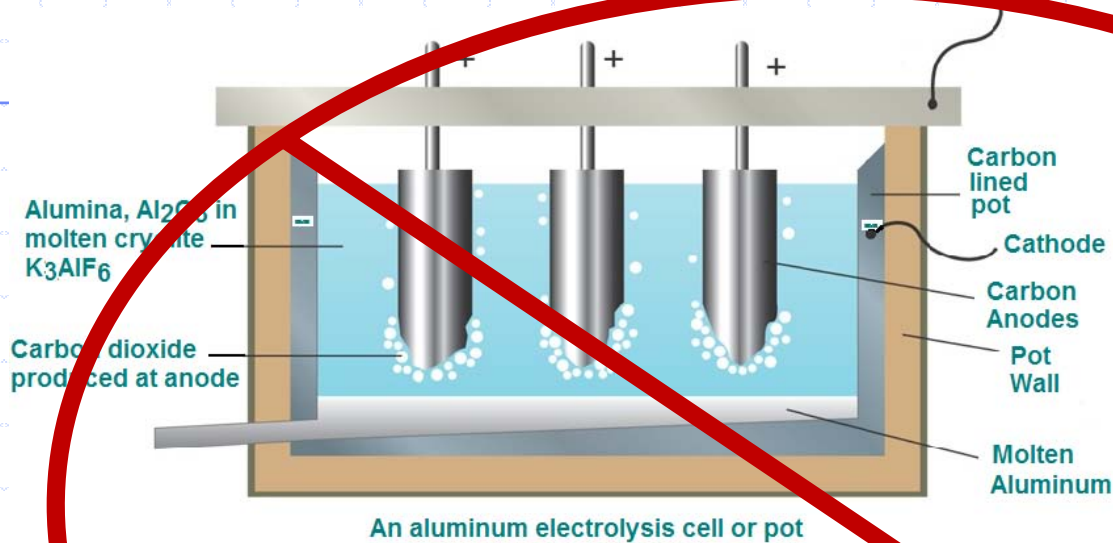


Hall-Heroult Process for Aluminum



- The alumina / cryolite mixture is electrolyzed using graphite electrodes.
- Aluminum forms at the cathode and oxygen at the anode.
- The oxygen reacts slowly with the carbon anode to produce carbon dioxide gas.

Hall-Heroult Process for Aluminum



Chemical reactions
in the processing of
aluminum

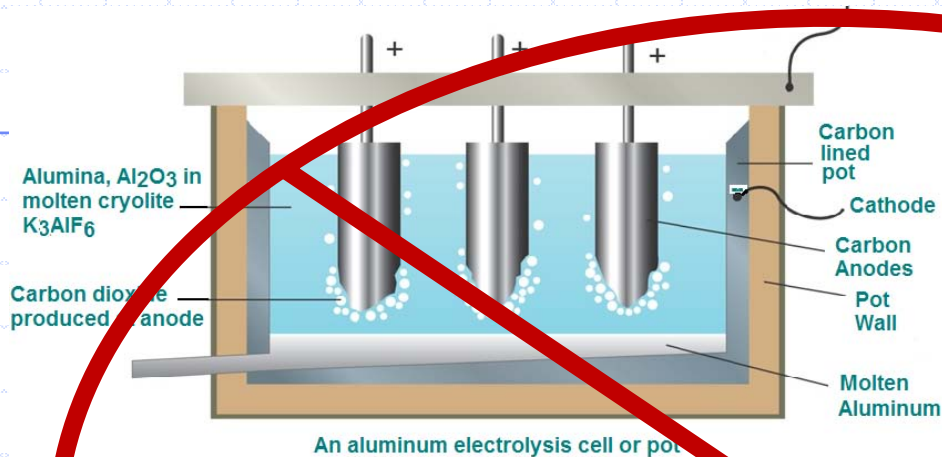
Alumina reacts with cryolite:



The overall cell reaction:



Hall-Heroult Process for Aluminum



The Hall-Heroult process produces aluminum that is about 99.5% pure.

- The aluminum produced by the Hall-Heroult process is about 99.5% pure. Large quantities of electricity are required to produce the aluminum.
- Aluminum electrolysis cells operate at a very low potential ranging from 4.0 to 5.5 volts but at an electrical current of 50,000 to 250,000 amperes.
- Each kilogram of aluminum requires between 13 and 16 kilowatt hours of electrical energy, in addition to the energy required to heat the alumina/cryolite mixture.



Chlor-Alkali Processes

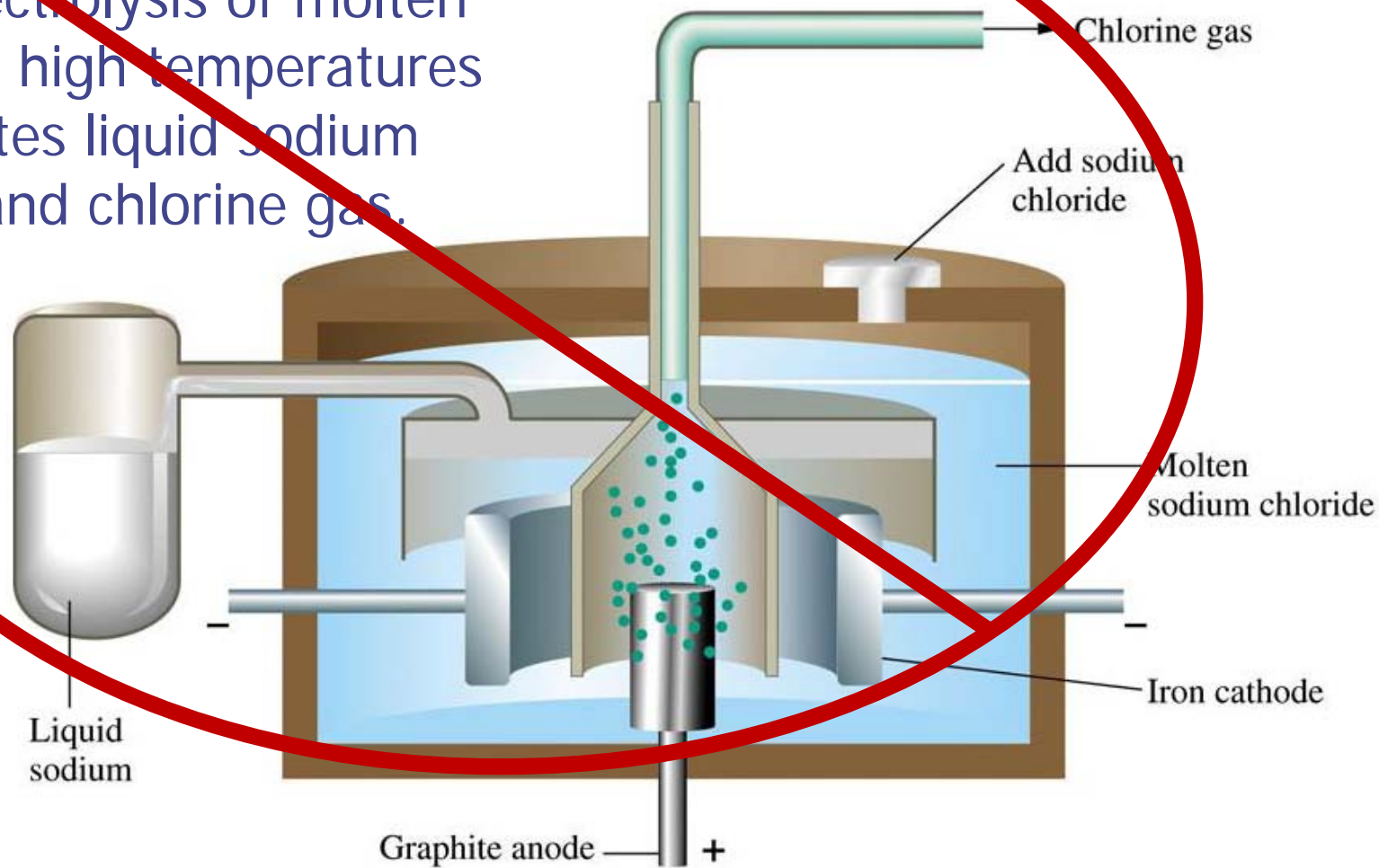
Electrolysis of Sodium chloride --

- ◆ With molten sodium chloride the products are liquid sodium and chlorine gas
- ◆ With aqueous sodium chloride or brine the products are sodium hydroxide (caustic soda) and chlorine gas.

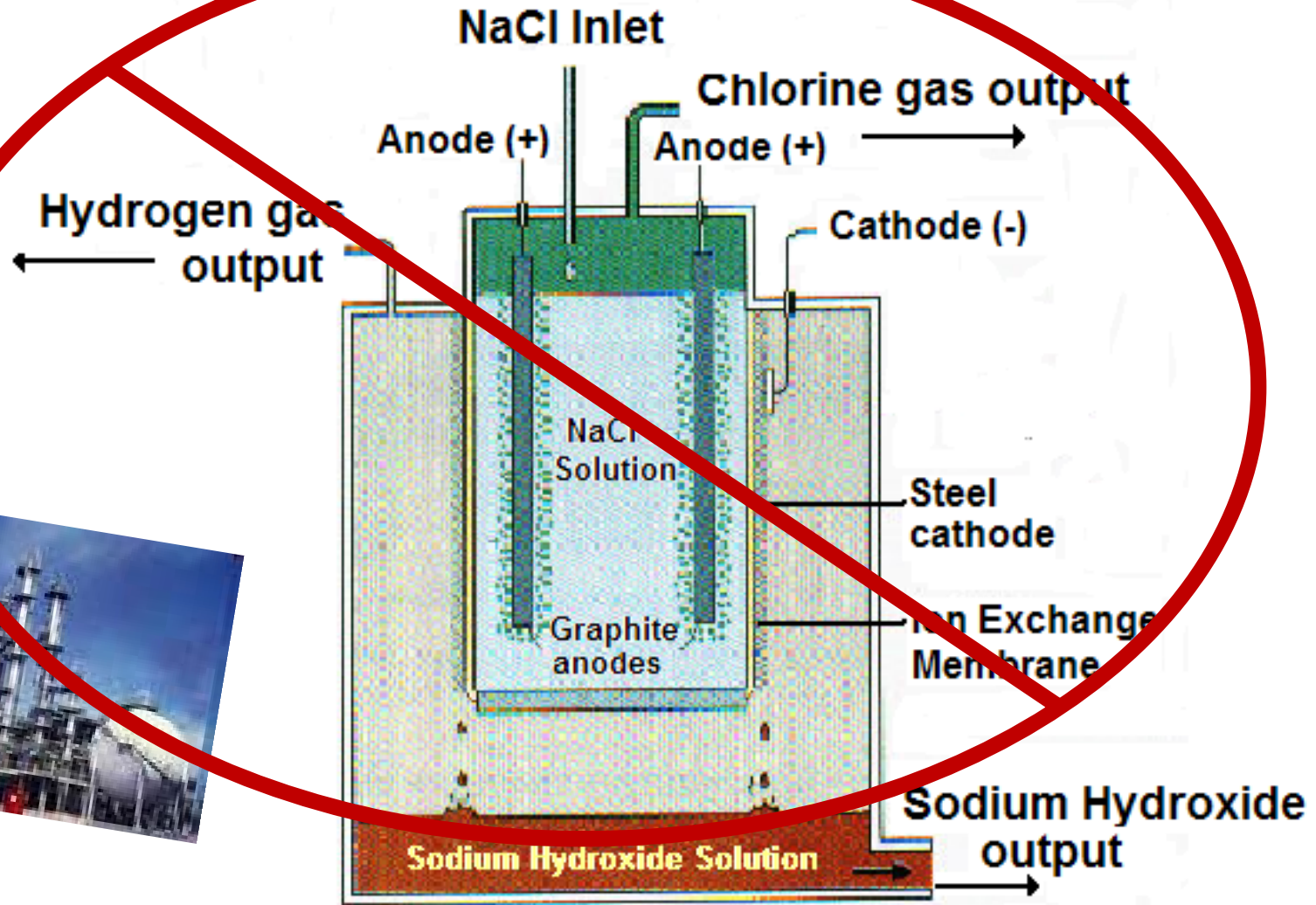


Electrolysis of Molten NaCl

The electrolysis of molten NaCl at high temperatures generates liquid sodium metal and chlorine gas.



Industrial Electrolysis of Brine

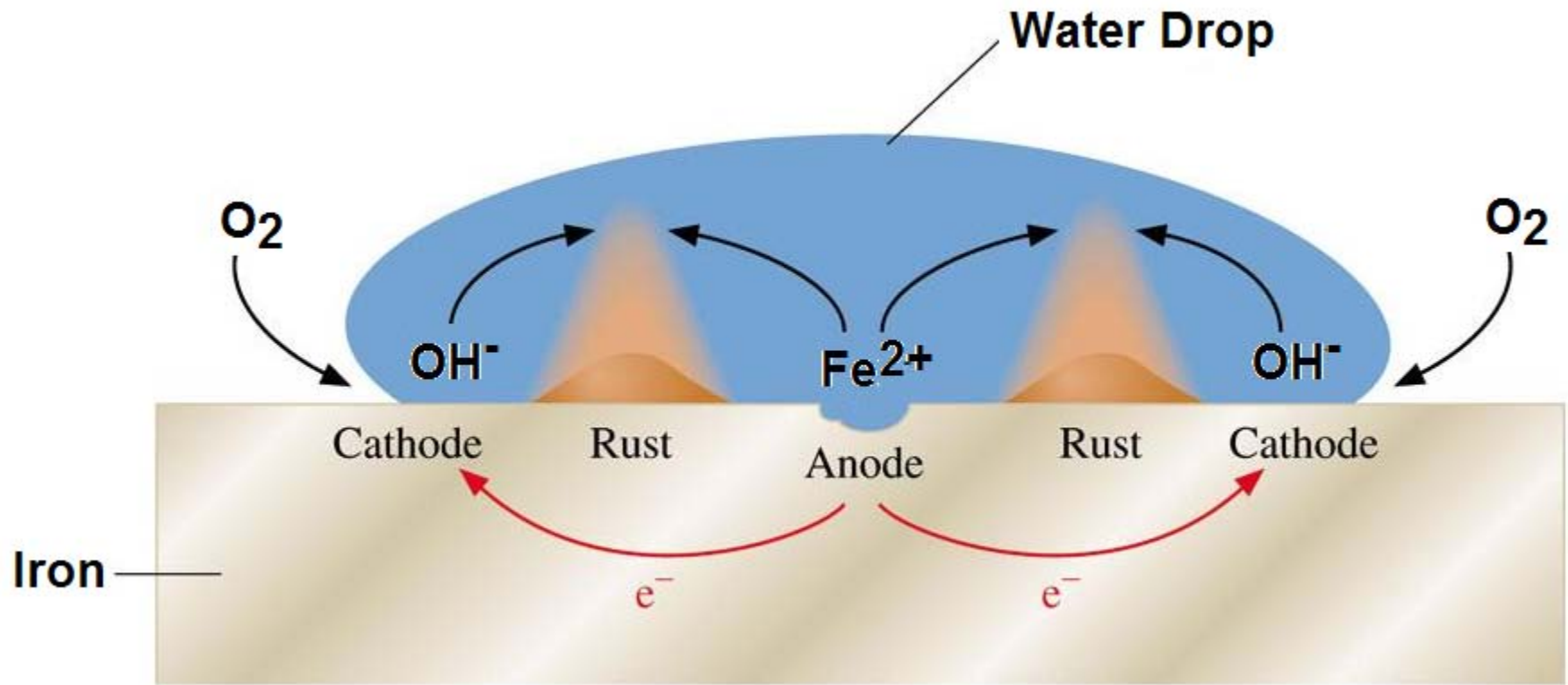


Corrosion

- ◆ Corrosion of metals is a common oxidation-reduction process in nature.
- ◆ The rusting of iron can be thought of as a form of an electrochemical cell.



Rusting of Iron



Rusting Iron



Rusting Process



Preventing Corrosion

- painting
- galvanizing
- sacrificial anode

